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A theoretical study of the cohesion of noble gases on graphite

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The interactions of the noble gases with a graphene sheet are investigated theoretically. The short range repulsive interaction between the noble gas and each carbon atom is described using Hartree-Fock atomic densities and a local density functional theory with the exchange functional corrected for the finite range of the interaction by introducing a Rae-type correction depending on the effective number of electrons. The long range interactions are introduced as the sum of the Axilrod-Teller triple-dipole interaction plus the dipole-dipole and dipole-quadrupole dispersive attractions damped according to the theory of Jacobi and Csanak. The energy arising from the interactions between the permanent quadrupoles on the carbon atoms with the dipole they induce on the noble gas is negligible, being nonzero only on account of the atomistic structure of graphene. The mobile and delocalized nature of the graphene π electrons causes the effective number of electrons to be around 500 rather than that of 12 appropriate for a system of entirely localized interactions with individual carbon atoms. Inclusion of the Axilrod-Teller term is required to obtain reliable predictions for the binding energies and equilibrium geometries. Absorption of a noble gas atom is predicted to occur at the site above the center of a six membered ring although this is preferred over two other sites by only about 5 meV. The methods presented for generating all the potentials can be applied to derive the interactions between any ion and carbon atom in the wall of a single-walled nanotube. Knowledge of these interactions is required to study the alkali halide nanocrystals encapsulated in single-walled carbon nanotubes of current interest. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2819242]

I. INTRODUCTION

The absorption of noble gases on graphite has been studied extensively both theoretically and experimentally over many years. Some investigations have focused on the behavior of an entire absorbed layer of atoms while others have been concerned with the process of absorption of just a single atom, in particular, the energetics and position of absorption. The relative simplicity of these systems makes them ideal for investigating the basic physics and chemistry of absorption. The review[1] presents an extended discussion and presentation of the experimental data as well as a theoretical review.

A partial motivation for the present study was to examine how the ideas, particularly those concerning electron correlation, that have provided good accounts of the binding of both ionic crystals[2–4] and the inert gas dimers,[5] transfer to the noble gas-graphite systems. However, the main objective of the present paper is to utilize the knowledge, both theoretical and especially experimental, provided by numerous previous investigations[1,6–14] of noble gas-graphite systems both to help gain understanding of and to develop theoretical models that can be applied to study the recently synthesized novel materials[15–19] consisting of ionic crystals encapsulated in single-walled carbon nanotubes. The structures of many of these crystals have been determined through newly developed techniques[20,21] in high resolution transmission electron microscopy (HRTEM). Many of the encapsulated crystals have structures related to those of the bulk material although exhibiting significant distortions. Some entirely novel structures[22] have also been observed. The first theoretical study[23,24] of the encapsulated KI used semiempirical interionic potentials dating from the 1970s (Ref. 25) while scaling semiempirical ion-wall interactions involving noble gases. This study did achieve its main aim of revealing the mechanism through which the tubes were filled by immersion in the molten salt. However, the experimentally observed structure could only be reproduced by assuming that the entire system of nanotube plus encapsulated salt was surrounded by the bulk salt during the microscopy. However, there was no surrounding salt during the HRTEM experiments used to determine the structures. Furthermore the structures of the encapsulated salts were shown to be unchanged on annealing.[26] A later density functional study[27] was also unable to correctly reproduce all the structural features, a failure hardly surprising in view of the inability of such approaches to describe the dispersive attractions. However, a very recent theoretical investigation[28] concerned with the smallest of the encapsulated crystals of both KI and CsI was able to reproduce the observed structures. This study also revealed the

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physical mechanisms causing the geometries of these nanocrystals to be driven away from the structures of bulk materials.

This investigation needed to be underpinned by a detailed understanding of the basic science underlying the interactions between all the atoms involved. The ability to derive all the interactions between the ions themselves has been provided by the extensive series of theoretical studies of bulk alkali halides.[2–4,29] Computations similar to those already documented in the literature have been performed for KI, RbI, and CsI.[30] The results of the present investigation both elucidate the factors governing the interactions between the ions and the wall carbon atoms and derive some of the required numerical data. This completes the acquisition of the background knowledge and expertise needed for theoretical investigations of the encapsulated alkali halide nanocrystals.

II. METHODOLOGY

A. Overview

The position of one noble gas atom with respect to the uppermost graphene sheet of solid graphite composed of an infinite number of such sheets is defined after specifying both the perpendicular distance z of the atom from the uppermost plane and an in plane vector $\mathbf{p}$ specifying the position at which the perpendicular from the atom crosses this plane. For one noble gas atom located at a position defined by coordinates z and $\mathbf{p}$, the total energy of interaction $U_T(z,\mathbf{p})$ is expressed as

$$U_T(z,\mathbf{p}) = U_{2B}(z,\mathbf{p}) + U_{\mathrm{AT}}(z,\mathbf{p}) + U_{\mathrm{QID}}(z,\mathbf{p}). \tag{1}$$

Here $U_{\mathrm{AT}}(z,\mathbf{p})$ is the total energy arising from the Axilrod-Teller triple-dipole dispersive interaction and $U_{\mathrm{QID}}(z,\mathbf{p})$ is the energy arising from the interaction between the permanent quadrupole moments of the carbon atoms with the dipole induced on the noble gas by these moments. In Eq. (1), $U_{2B}(z,\mathbf{p})$ is the total energy arising from the two-body interactions, so that this is given by

$$U_{2B}(z,\mathbf{p}) = \sum_i V(r_i), \tag{2}$$

where the sum is over all carbon atoms in the graphite and $V(r_i)$ is the energy of interaction of the noble gas atom with one carbon atom located at a distance r_i. The GULP program,[31] used both in this paper to evaluate the total energy $U_T(z,\mathbf{p})$ and in the study[28] of the encapsulated iodide nanocrystals, requires that all two-body potentials depend only on the single variable r.

The interaction $V(r)$ is composed of the contribution $V_s^0(r)$ which would arise in the absence of electron correlation plus two correlation terms $V_s^{\mathrm{corr}}(r)$ and $V_{\mathrm{disp}}(r)$ so that

$$V(r) = V_s^0(r) + V_s^{\mathrm{corr}}(r) + V_{\mathrm{disp}}(r). \tag{3}$$

Both the uncorrelated energy $V_s^0(r)$ and the first of the two correlation contributions are labeled with the subscript s to denote that these interactions are of short range in that they depend explicitly on the overlapping of the electron densities of the noble gas and carbon atoms and vanish at distances r which are sufficiently large that this overlap becomes negligible. The last correlation contribution $V_{\mathrm{disp}}(r)$, that arising from the dispersive attraction of the two atoms, is of long range in that it does not vanish for those r at which the overlap becomes negligible but has there a leading term varying as r^{-6}.

Both the Axilrod-Teller $(U_{\mathrm{AT}}(z,\mathbf{p}))$ and the permanent quadrupole-induced-dipole $(U_{\mathrm{QID}}(z,\mathbf{p}))$ terms in Eq. (1) are many-body interactions, with the latter not arising from electron correlation but being captured by Hartree-Fock theory. Consequently, the only two-body correlation terms are $V_s^{\mathrm{corr}}(r)$ and $V_{\mathrm{disp}}(r)$. Although fundamental theory[32] does indicate that these are conceptually different and distinct contributions, the question arises as to whether any double counting of these two terms is introduced if $V_s^{\mathrm{corr}}(r)$ is evaluated using a local density approximation based on the density functional theory (DFT) of a uniform electron gas. However, a theoretical argument due to Rae[33] as well as extensive investigations of the noble gas dimers[33–36] and ionic solids[2,29] using uniform electron-gas DFT to evaluate both $V_s^0(r)$ and $V_s^{\mathrm{corr}}(r)$ have provided very strong evidence that any double counting introduced by this approach is only, at worst, minimal. Furthermore, for a range of ionic crystals, this conclusion has been substantially reinforced by more recent extensive studies[2–4,37–41] in which the accuracy was improved by replacing the DFT evaluation of $V_s^0(r)$ by one yielding a result that is exact once given the wavefunctions of the two interacting atoms or ions. However, the noble gas dimers provide a much more severe test of the evaluation of the correlation energy because, for these systems, this energy provides the only attraction so that the total cohesive energies lie in the $10^{-3}-10^{-4}$ a.u. range. This contrasts with the ionic crystals, where it might be *a priori* plausible, that any errors in the correlation terms could be overshadowed by the much larger Madelung and uncorrelated short range interactions. These latter two cause the total binding energies to be much larger, lying typically in the 0.25–1 a.u. range. However, in a very recent study[5] of the noble gas dimers, the binding energies and equilibrium interatomic separations predicted from Eq. (3), with $V_s^0(r)$ evaluated essentially exactly through Hartree-Fock electronic structure computations, agreed well with experiment. This provides further compelling evidence to reinforce the conclusion that the correlation energy can be reliably calculated as the sum of the uniform electron-gas DFT term plus the dispersive attractions provided that the latter are suitably damped at those separations at which the overlap of the electron densities of the two species is not negligible.

The GULP program was used to compute the total energy $U_T(z,\mathbf{p})$ as a function of z for three different values of $\mathbf{p}$. These are above the center of one of the six membered rings ($\mathbf{p}=H$), directly above one carbon atom ($\mathbf{p}=T$), and above the center of one of the carbon-carbon bonds ($\mathbf{p}=B$). This program calculates $U_{\mathrm{AT}}(z,\mathbf{p})$ given the values for the Axilrod-Teller coefficients. It uses the shell model[42] to compute the permanent quadrupole-induced-dipole energy $U_{\mathrm{QID}}(z,\mathbf{p})$ after specification of the parameters as described below in Sec. II C 2.

B. The dispersive interactions

1. Definitions and dispersion damping

The two-body dispersive attraction $V_{\mathrm{disp}}(r)$ between the gas atom (A) and one carbon (C) is given by

$$V_{\mathrm{disp}}(r) = -\chi_{\mathrm{AC}}^{\mathrm{DD}}(r)\mathrm{C}_6(\mathrm{AC})r^{-6} - [\chi_{\mathrm{AC}}^{\mathrm{DQ}}(r)\mathrm{C}_8^{\mathrm{DQ}}(\mathrm{AC}) + \chi_{\mathrm{AC}}^{\mathrm{QD}}(r)\mathrm{C}_8^{\mathrm{QD}}(\mathrm{AC})]r^{-8} \tag{4}$$

when the leading instantaneous dipole-induced dipole (DD) and dipole-quadrupole terms are retained. The first of the latter is the interaction (DQ) arising from the interaction of the quadrupole induced on the carbon by an instantaneous dipole on the gas atom with the second (QD) originating from the dipole induced on the carbon by an instantaneous quadrupole on the gas. In Eq. (4) $\mathrm{C}_6(\mathrm{AC})$, $\mathrm{C}_8^{\mathrm{DQ}}(\mathrm{AC})$, and $\mathrm{C}_8^{\mathrm{QD}}(\mathrm{AC})$ are the standard dispersion coefficients governing these three interactions. The quantities $\chi_{\mathrm{AC}}^{\mathrm{DD}}(r)$, $\chi_{\mathrm{AC}}^{\mathrm{DQ}}(r)$, and $\chi_{\mathrm{AC}}^{\mathrm{QD}}(r)$ are damping functions, having values between zero and 1, which are unity for distances r where the overlap of the electron densities of the atoms A and C is negligible but which take smaller values at those r for which this overlap becomes appreciable.

In the theory of Jacobi and Csanak,[43] each dispersion damping function depends on two damping parameters, one, d_{C}, for the carbon atom plus another, d_{A}, for the noble gas. The damping parameter for any atom X was calculated from the result of the Lassettre theory[44]

$$d_{\mathrm{X}} = \sqrt{2}[\sqrt{I_{\mathrm{X}}} + \sqrt{(I - \Delta E_{\mathrm{X}})}], \tag{5}$$

with all quantities expressed in a.u. Here I_{X} is the ionization potential of the ground state of atom X with ΔE_{X} being the energy of the longest wavelength dipole allowed transition, this being to the $np^5(n+1)s\ ^1P$ and $2s^22p3s\ ^3P$ states of the noble gases and carbon, respectively. The required energies were taken from Moore.[45]

The Jacobi and Csanak theory provides the fundamental expressions from which explicit forms, depending only on r and the two damping parameters, can be derived. Since only the function for a homonuclear pair was explicitly presented,[43] the three functions appearing in Eq. (4) had to be derived subsequently,[2,3] these being most conveniently presented in the appendix to the recent paper.[5]

2. The dipole-dipole and three-body dispersion coefficients

Fundamental quantum mechanical theory yields the expression

$$\mathrm{C}_6(\mathrm{AC}) = \left(\frac{3}{\pi}\right)\int \alpha_{\mathrm{A}}(iE)\alpha_{\mathrm{C}}(iE)dE \tag{6}$$

for the dipole-dipole dispersion coefficient $\mathrm{C}_6(\mathrm{AC})$,[46] where $\alpha_{\mathrm{X}}(iE)$ is the dipole polarizability at imaginary frequency for atom X. The $\mathrm{C}_3(\mathrm{AGr})$ coefficient yields, as $-\mathrm{C}_3(\mathrm{AGr})/z^3$, the long range dipole-dipole dispersive attraction between an atom A located at perpendicular distance z above the top layer of a graphite sample of infinite extent when this is regarded as a structureless medium characterized solely by its energy dependent dielectric function $\varepsilon(iE)$. The $\mathrm{C}_3(\mathrm{AGr})$ coefficient is related to $\alpha_{\mathrm{A}}(iE)$ and the corresponding quantity for graphite $g_{\mathrm{Gr}}(iE)$, which is a function of only $\varepsilon(iE)$, by[8,47]

$$\mathrm{C}_3(\mathrm{AGr}) = \frac{1}{4\pi}\int g_{\mathrm{Gr}}(iE)\alpha_{\mathrm{A}}(iE)dE. \tag{7}$$

In the atomistic description of graphite, summation over all the graphite carbon atoms of the interaction $-\mathrm{C}_6(\mathrm{AC})/r_{\mathrm{AC}}^6$ between each such atom and the atom A shows that $\mathrm{C}_3(\mathrm{AGr})$ is related to $\mathrm{C}_6(\mathrm{AC})$ through[8,11]

$$\mathrm{C}_3(\mathrm{AGr}) = \frac{\rho\pi\mathrm{C}_6(\mathrm{AC})}{6} = \frac{\pi\mathrm{C}_6(\mathrm{AC})}{3a_sd}. \tag{8}$$

Here ρ is the atomic density which can be expressed in terms of the base area as of a unit cell and intersheet distance d as $2/a_sd$.

For many interactions, neither the atomic polarizability $\alpha_{\mathrm{A}}(iE)$ nor the function $g_{\mathrm{Gr}}(iE)$ for the solid is known as a function of energy. These are not currently available either for the vast majority of the ions composing the alkali halides or for single-walled carbon nanotubes. Limitations of this kind motivated the development of tractable yet accurate approximations to the integrals in Eqs. (6) and (7) most of which depend on two parameters, one most commonly being the static dipole polarizability. This quantity is more readily available, being known from experiment for the noble gases and for the ions in many crystals from a combination of theory and experiment as discussed in the review.[29] One widely used approximation for dipole-dipole dispersion coefficients, the Slater-Kirkwood formula,[48] is best regarded[49] as the result generated when Eq. (6) is evaluated using a two point Padé approximation to both the $\alpha_{\mathrm{X}}(iE)$. The resulting expression

$$\mathrm{C}_6(\mathrm{AC}) = \frac{3}{2}\frac{\alpha_{\mathrm{A}}\alpha_{\mathrm{C}}}{(\alpha_{\mathrm{A}}/P_{\mathrm{A}})^{1/2} + (\alpha_{\mathrm{C}}/P_{\mathrm{C}})^{1/2}} \tag{9}$$

provides a rigorous upper bound to $\mathrm{C}_6(\mathrm{AC})$ if each P_{X}, the electron number of species X, is taken to be the total number of electrons on that species.[49] However, not surprisingly in view of the result that just the most loosely bound electrons are responsible for the vast majority of the polarizability,[50,51] this bound is so lose as to be of little practical value. Nevertheless, it has been shown[2] that the predictions of Eq. (9) are correct to within about 20% provided that each P_{X} is taken to be the number of most loosely bound electrons, either 6 or 8 for a noble gas, unity for hydrogen or an alkali metal, and 2 for an alkaline earth. The least satisfactory result for the cases examined was that of $\mathrm{C}_6(\mathrm{NeNe})$ for which the prediction of Eq. (9) is 33% too large if P_{Ne} is taken to be 8. Furthermore, it was shown that, after deriving the electron number for species X by demanding that Eq. (9) reproduces the exact $\mathrm{C}_6(\mathrm{XX})$ coefficient from the exact polarizability α_{X}, the values of $\mathrm{C}_6(\mathrm{XY})$ for the heteronuclear pairs predicted from Eq. (9) were correct to within 5%. It was further shown that this result extended to pairs for which neither P_{X} nor P_{Y} had been thus derived if each electron number was calculated from the isoelectronic noble gas. The exact polarizabilities and $\mathrm{C}_6(\mathrm{AA})$ coefficients for the noble gases are

TABLE I. Noble gas parameters and coefficients of purely dipolar dispersive interactions (a.u.).

A	α_A[a]	$C_6(AA)$[b]	P_A[c]	$C_6(AC)$			d_A	ν (CCA)	
				See text	Eq. (13)[d]	Eq. (13)[e]	Eq. (5)	Eq. (14)	Ref. 13
Ne	2.676	6.93	4.455	8.547	10.32	9.82	1.855	66.85	58.6
Ar	11.096	68.5	6.106	36.652	35.30	34.71	1.623	261.76	214.7
Kr	16.753	139.0	7.305	54.046	50.71	48.26	1.540	388.12	312.8
Xe	27.318	301.0	7.901	85.987	75.13	69.71	1.438	608.96	479.9

[a] α_A from Ref. 52 Ne; from Ref. 75 Ar; from Ref. 76 He Kr, and Xe.
[b] Reference 36.
[c] Reference 2.
[d] Calculated using the α_A C_6 (AA) in this table.
[e] From Ref. 24 calculated using slightly different values for α_A and C_6 (AA).

presented in Table I together with the electron numbers derived from Eq. (9). However, the lack of prior knowledge of the carbon electron number, which plausibly could lie anywhere between 1 and 4, prevents the immediate derivation of the $C_6(AC)$ coefficients from Eq. (9). The coefficients in the fourth numerical column of Table I were therefore calculated as $4\varepsilon\sigma^6$ from the well depths (ε) and distances (σ) derived[10] using both combining rules[9] and a semiempirical analysis of experimental data.

The $C_6(AC)$ values calculated by taking these to be equal to the coefficient of r^{-6} in a semiempirically determined Lennard-Jones potential should not be accepted without further examination. Although it is most likely that all of the short range terms including the reduction $[1-\chi_{AC}^{DD}(r)]C_6(AC)r^{-6}$ of the undamped dipole-dipole dispersive attraction are included in the Ar^{-12} repulsive term, it is *a priori* unclear as to how the effects of the dipole-quadrupole dispersive attractions are incorporated in a Lennard-Jones potential. A partial assessment of the reliability of the $C_6(AC)$ values presented in the fourth column of Table I is provided by the predictions of the $C_3(AGr)$ coefficients derived from an approximate yet physically realistic approximation to the integral in Eq. (7). In this approximation, the energy dependence of both $g_{Gr}(iE)$ and $\alpha_A(iE)$ is expressed in the form

$$\alpha_A(iE)=\alpha_A\left(1-\left(\frac{E}{E_A}\right)^2\right), \tag{10}$$

$$g_{Gr}(iE)=g_{Gr}\left(1-\left(\frac{E}{E_{Gr}}\right)^2\right). \tag{11}$$

These relations ensure that both the asymptotic behaviors at large E and the value of $\alpha_A(iE)$ at $E=0$ are correctly reproduced. Substitution of Eq. (10) into the expression provided by Eq. (6) with C replaced by A yields

$$C_6(AA)=\tfrac{3}{4}\alpha_A^2E_A. \tag{12}$$

For each noble gas, the value of E_A is derived by demanding that Eq. (12) reproduces the exact value of the $C_6(AA)$ coefficient from the exact polarizability α_A. Substitution of the relations (10) and (11) into Eq. (7) yields the result[8]

$$C_3(AGr)=\frac{g_{Gr}\alpha_AE_{Gr}E_A}{8(E_{Gr}+E_A)}, \tag{13}$$

from which the $C_6(AC)$ coefficients can be calculated from Eq. (8) after invoking the values $a_s=5.24$ Å and $d=3.37$ Å.[8] The values of g_{Gr} and E_{Gr} presented in Table II were derived by fitting the experimentally measured function $g_{Gr}(iE)$ to Eq. (11).[8] The predictions for $C_6(AC)$ presented in the fifth numerical column of Table I, which were derived from Eqs. (8), (12), and (13) using Table I α_A and $C_6(AA)$ values, confirm that the results presented in the preceding column are indeed reasonable. The sixth numerical column of that table shows that the results previously derived[8] from Eq. (13) using slightly different values of α_A and $C_6(AA)$ are only marginally smaller than those predicted from the noble gas data of Table I.

The polarizability of an isolated carbon atom is known from very accurate *ab initio* electronic structure computations to be 11.83 a.u.[52] This is very similar to the mean polarizability of 10.26 a.u. (Table II) for a carbon atom in graphite. This latter value is calculated as the appropriate average of the parallel and perpendicular components of the polarizability. These were derived from a combination of experimental studies of the dielectric properties of graphite with a semiempirical analysis of its measured compressibility.[6,7] Substitution into Eq. (9) of both this 10.26 a.u. result and the $C_6(XeC)$ coefficient presented in the fourth column of Table I allows a value of 1.118 to be deduced for the carbon electron number. This, coupled with the value for α_C provides all the data needed to derive the dipole-dipole dispersion coefficients for the ions in the alkali

TABLE II. Carbon and graphite parameters (a.u.).

α_C	P_C	g_{Gr}[a]	E_{Gr}[a]	d_C	$\langle r^2\rangle_C$	$\langle r^4\rangle_C$	Q_{zz}[b]
10.26	1.118	0.73	0.5218	1.437	3.890	35.143	−1.08

[a] Reference 8.
[b] See text.

TABLE III. Dipole-quadrupole dispersion coefficients and dependent parameters (a.u.).

A	$\langle r^2\rangle_A$[a]	$\langle r^2\rangle_A$[a]	$C_8^{DQ}(AC)$	$C_8^{QD}(AC)$	$C_8(AC)$[b]	$C_8(AC)$[c]	$C_8(AC)$[d]
			Present work, Eq. (17)			Previous work	
Ne	7.370	23.462	115.823	40.813	156.6	20.3	75.4
Ar	19.851	125.395	496.682	347.286	844.0	132.7	493.3
Kr	26.549	209.331	732.393	639.205	1371.6	220.1	763.8
Xe	37.004	381.196	1165.234	1328.690	2493.9	388.9	1231.7

[a] Reference 59.
[b] Sum of the two previous columns.
[c] Reference 11.
[d] Reference 12.

iodides interacting with the atoms composing the walls of carbon nanotubes. The coefficient $C_6(XeC)$ was chosen to derive P_C because the iodide-carbon interaction is the largest ion-wall dispersive attraction encountered for the encapsulated alkali iodides.

The coefficients $\nu(CCA)$ determining the strength of the Axilrod-Teller triple-dipole interaction[53,54] were derived from the Midzuno-Kihara formula.[55] Here, this takes the form

$$\nu(\mathrm{CCA}) = \frac{S_C S_A (2S_C + S_A)}{(S_C + S_A)^2}, \tag{14}$$

where

$$S_C = C_6(\mathrm{CC})\alpha_A, \tag{15}$$

$$S_A = \frac{C_6(\mathrm{AA})\alpha_C^2}{\alpha_A}. \tag{16}$$

The required value of $C_6(CC)$ was calculated from the Slater-Kirkwood formula using the carbon data assembled in Table II. The results presented in the eighth numerical column of Table I are not excessively larger than those previously derived[13] from a different approximate theory and reported in the last column of this table. The firm foundations of the Midzuno-Kihara formula, coupled with the result that for other closed shell systems, it has been shown to be accurate to within 5%,[51] show that there are no reasons to prefer the earlier results in the last column of Table I over those predicted from Eq. (14).

3. The dipole-quadrupole dispersion coefficients

The dipole-quadrupole dispersion coefficients were calculated from the Starkschall-Gordon formula[56]

$$C_8^{DQ}(\mathrm{AC}) = \frac{3}{2}\frac{C_6(\mathrm{AC})\langle r^4\rangle_C}{\langle r^2\rangle_C} \tag{17}$$

with the appropriate electronic expectation values, presented in Table II, derived by considering just the outermost electrons. For the noble gases, only the six most loosely bound electrons were included as justified elsewhere.[57] The values for carbon are those for a single electron in the $2p$ orbital. This latter is consistent both with the result that the electron number derived from the Slater-Kirkwood formula is close to unity and the idea that the majority of the polarizability of graphite originates from the π electrons. The carbon expectation values were computed from the $(2J+1)$ weight extended average level computation[58] for the ground manifold of the carbon atom. Those for the noble gases were taken from the extensive tabulation.[59] The values of the quadrupole-dipole coefficients $C_8^{QD}(AC)$ are derived by replacing in Eq. (17) the carbon expectation values by those of the noble gas (Table III).

Two different sets of values for the $C_5(AGr)$ coefficients have been derived previously.[11,12] These can be related to the $C_8(AC)(=C_8^{DQ}(AC)+C_8^{QD}(AC))$ coefficient of the atomistic description by a procedure exactly analogous to that already described for the dipole-dipole dispersive attractions. The required relation is[11]

$$C_5(\mathrm{AGr}) = \frac{\rho\pi C_8(\mathrm{AC})}{15} = \frac{2\pi C_8(\mathrm{AC})}{15 a_s d}. \tag{18}$$

The resulting values for $C_8(AC)$ not only significantly differ from each other but are also much less than those predicted by the Starkschall-Gordon formula. Even though it is stated in the latter work[12] that the earlier values[11] should be disregarded, there are no reasons to prefer the latter set over the present Starkschall-Gordon predictions. Since, for a wide range interacting pairs, this formula has been shown[2] to predict the dipole-quadrupole dispersion coefficients with an error no greater than 30% at most, it is difficult to believe that this underestimates the $C_8(AC)$ coefficients by a factor of 3.

C. The shorter range interactions

1. Overlap dependent short range interactions

Each of the uncorrelated short range interactions $V_s^0(r)$ is calculated by the method introduced by Massey and Sida[60] with subsequent refinements. In this approach, the electron density of the interacting pair is expressed as the sum of the Hartree-Fock densities of the atoms. The differences between the contributions from the electron kinetic energies and electron exchange $(V_{ex}(r))$ in the interacting and noninteracting pairs are calculated using DFT of an electron gas of uniform density and infinite extent. The Coulombic contribution to $V_s^0(r)$, that is the energy of the purely electrostatic interaction that would arise in the absence of interatomic electron exchange, is calculated exactly. The much later addition of an electron correlation contribution computed using the same DFT assumptions produces the method used extensively by Gordon and Kim.[61]

Although the first applications of this DFT method to the noble gas dimers[61] and ionic crystals[62] yielded results which agreed well with experiment, it later emerged that such agreements were partially fortuitous because the absence of the dispersive attractions tended to be canceled by overestimations of the magnitudes of the exchange contributions $V_{ex}(r)$. Rae[33,34] showed that $V_{ex}(r)$ is too large in magnitude when calculated using the functional for an electron gas of infinite extent and that it should be multiplied by a factor $\gamma(N)$, lying between zero and 1, which depends on the effective number (N) of electrons contributing significantly to the exchange interaction. Subsequent investigations[35,36] showed that N should be taken to be the total number of outermost electrons on both atoms and that three other possibilities, the number of outermost electrons on just one atom and the total number of electrons on either one or both atoms, should be rejected. The choice of either the total number of electrons or just the number of outermost electrons on only one atom can be seen[36] to be erroneous because the former predicts that the exchange contribution, $\gamma(N)V_{ex}(r)$, to the interaction of two helium atoms is zero while the latter extends this incorrect prediction of zero $\gamma(N)V_{ex}(r)$ to the interactions of all pairs in which both atoms have only two outermost electrons. The comparison[63] between the DFT predictions of $V_s^0(r)$ with those calculated exactly using the same dimer electron density provided the most direct demonstration that N should be taken to be the total number of outermost electrons on both atoms. A more extensive review of a number of different types of refinement to the Massey and Sida DFT is presented in Sec. 8 of Ref. 29.

An atom located over the center of a six membered ring, that is one with coordinate $\mathbf{p}=H$, interacts simultaneously with at least six carbon atoms. This observation taken together with the semiconducting nature of graphite shows that the choice of 12 for N, that would be correct for a noble gas carbon atom dimer, needs to be reexamined. In the event that the single noble gas atom interacted with a very large, effectively infinite, piece of metal, the total exchange energy of the entire system of atom plus metal would clearly be evaluated by using the standard DFT expression for an electron gas of infinite extent. This means that N would be taken to be infinity. However, the existence of even the smallest nonuniformity of the electron density would enable this to be expressed, at least formally, as the sum of contributions from the individual atoms. The total exchange energy could then be expressed as a sum of contributions from one-body, two-body, and higher order multibody terms. Since this is an expansion of the original expression for the exchange energy in a series, the same infinite value of N would be retained in all the terms including the dominant two-body interactions. Although the electrons in a semiconductor are less mobile than those in a metal, they will not be so localized that the system of noble gas plus graphene sheet could be approximated as an isolated system consisting of the noble gas plus, for example, when $\mathbf{p}=H$, just the six closest carbon neighbors in which case the appropriate value for N would be 32. Clearly, the correct N value for the atom plus infinite graphene sheet must be great than 32 but less than the infinite value appropriate for a metal. Such an intermediate value must reflect the fact that the effects of a perturbation of the density at any position in a graphene sheet must decay with increasing distance from the location of the perturbation. It is an important objective of the present paper to investigate the correct value to be used for N in the computation of the interaction of a noble gas atom with graphite.

The short range correlation contribution $V_s^{\mathrm{corr}}(r)$ to the total short range two-body interaction $V_s(r)$ is calculated from the DFT of a uniform electron gas of infinite extent, that is by the method introduced by Gordon and Kim.[61] However, in contrast to the viewpoint originally adopted,[61] the term $V_s^{\mathrm{corr}}(r)$ is introduced here solely as an approximation to electron correlation effects of short range, it being recognized, as discussed in Sec. II A above, that the total two-body correlation energy contains in addition the dispersive attractions.

2. The permanent quadrupole-induced-dipole interaction

The concentration of π-electron charge above and below, but not in the plane, of a graphene sheet causes each carbon atom to carry a permanent electric quadrupole moment of negative sign. The interactions between these quadrupole moments have been shown to play a significant role in determining the interactions between and stacking of these sheets in graphite.[14] This work also demonstrated that the carbon quadrupoles play a significant role in the absorption by graphite of both water and nitrogen gas. The attractive interaction between a cation and the negatively charged end of these carbon quadrupoles is the essential factor in the binding of such ions above the rings of aromatic hydrocarbons. The review[64] documents the widespread occurrence of such cation-π interactions.

The significance of the carbon quadrupole moment, demonstrated by its role in the three types of interaction just mentioned, motivates investigating the importance of this carbon property in the binding of noble gas atoms to graphite. Any such binding would arise through a quadrupole-induced-dipole interaction caused by the attraction of the permanent quadrupoles on the carbon atoms to the dipole induced on the noble gas by the permanent electric field resulting as the sum of all the fields created by the carbon quadrupoles. A review[14] of the quadrupole moment per atom in benzene, naphthalene, and anthracene suggested that the zz component (Q_{zz}) in graphite should be taken to be −0.973 a.u. The similar value of −1.08 a.u. is derived from the molecular quadrupole yielded by a second order Möller-Plesset computation for benzene.[65] In the present work, the quadrupole moment on each carbon atom was modeled by a linear arrangement of three charges. A charge of 1 a.u. was placed at the position of the nucleus while locating a negative charge of 0.5 a.u. at a distance of 1.039 a.u. above and below the plane to ensure that the latter value of Q_{zz} was reproduced. The shell model was used to introduce the polarizability of the noble gas. This model requires for atom A a shell charge (Y_A) and a quadratic force constant k_A which determine the polarizability α_A as Y_A^2/k_A. The natural choice

TABLE IV. Comparison of computed and analytic quadrupole-induced-dipole energies. Energies in a.u. and distances z in Å. For definitions of fields see text.

	z	H		B		T	
		Analytic	GULP	Analytic	GULP	Analytic	GULP
Ar	3.0	-5.5×10^{-10}	-1.4×10^{-6}	-2.6×10^{-7}	-1.3×10^{-7}	-6.2×10^{-7}	-4.3×10^{-7}
	3.7	-5.4×10^{-7}	-3.2×10^{-8}	-1.1×10^{-7}	-2.9×10^{-9}	-3.6×10^{-8}	-1.6×10^{-8}
Xe	3.0	-1.3×10^{-9}	-3.6×10^{-6}	-6.6×10^{-7}	-3.2×10^{-7}	-1.5×10^{-6}	-1.0×10^{-6}
	3.7	-1.3×10^{-6}	-1.0×10^{-7}	-2.7×10^{-7}	-7.0×10^{-9}	-8.7×10^{-8}	-4.1×10^{-8}

$(-P_A)$ of the negative of the electron number (Table I) for each shell charge allows k_A to be determined by demanding that the polarizability is reproduced.

III. RESULTS AND DISCUSSION

A. The quadrupole-induced-dipole energy

The significance of the quadrupole-induced-dipole energy $U_{\mathrm{QID}}(z,\mathbf{p})$ was investigated through computations with the GULP program using the shell model for the noble gas polarizability and introducing carbon quadrupoles only on a single graphene sheet as described in Sec. II C 2. These computations show that for all but unreasonably short values of z, the energies $U_{\mathrm{QID}}(z,\mathbf{p})$ are so small as to be negligible. Typical numerical values are reported in Table IV.

The negligibly small values of $U_{\mathrm{QID}}(z,\mathbf{p})$ can be understood by performing an analytic calculation in which the interactions between the noble gas and the closest carbon atoms are treated exactly while approximating more distant carbon atoms as a continuous distribution of quadrupoles. For the three positions H, B, and T defined in Sec. II A, symmetry shows that the electric field (F), created at the noble gas as the sum of those generated by all the quadrupoles, is directed along the z direction. The energy $U_{\mathrm{QID}}(z,\mathbf{p})$, given by the first term in Eq. (40) of Ref. 66, is

$$U_{\mathrm{QID}}(z,\mathbf{p}) = \tfrac{1}{2}\alpha_A F^2. \tag{19}$$

The z component, F_i, of the field created by a carbon quadrupole moment located at a distance R_i from the noble gas is derived from the third term of Eq. (41a) of Ref. 66. The result is

$$F_i = Q_{zz}\frac{3}{2}\frac{\cos\theta_i(5\cos^2\theta_i - 3)}{R_i^4}, \tag{20}$$

with

$$\cos\theta = \frac{z}{R_i} = \frac{z}{\sqrt{(z^2+s_i^2)}}, \tag{21}$$

where s_i is the distance between carbon atom i and the point (O) at which the perpendicular from the position of the noble gas intersects the graphene sheet. Since, in one graphene sheet, there are two carbon atoms per unit cell of area $\frac{3}{2}R_{\mathrm{CC}}^2\sqrt{3}$, the density of quadrupoles ρ_Q in the continuum description is given by

$$\rho_Q = \frac{4Q_{ZZ}}{3R_{\mathrm{CC}}^2\sqrt{3}}, \tag{22}$$

where R_{CC} is the carbon-carbon bond distance taken to be 1.418 Å. The total quadrupole moment in a circular annulus lying between s and $s+ds$ from O is given by $2\pi s\rho_Q ds$. The electric field $F^{\mathrm{C}}(s_m s_u)$ created at the noble gas by a continuous distribution of quadrupoles lying in a finite circular ring, with minimum and upper radii s_m and s_u, respectively, is found from Eq. (20) to be given by

$$F^{\mathrm{C}}(s_m s_u) = 2\pi\rho_Q\left(\frac{3}{2}\right)\int_{s_m}^{s_u}\frac{zs}{(z^2+s^2)^{5/2}}\left(\frac{5z^2}{z^2+s^2} - 3\right)ds \tag{23}$$

$$= 3\pi\rho_Q z\left(\frac{s_u^2}{(z^2+s_u^2)^{5/2}} - \frac{s_m^2}{(z^2+s_m^2)^{5/2}}\right). \tag{24}$$

This result reduces, in the limit that upper radius s_u tends to infinity, to

$$F^{\mathrm{C}}(s_m\infty) = -3\pi\rho_Q z\frac{s_m^2}{(z^2+s_m^2)^{5/2}}. \tag{25}$$

For the noble gas atom positions H, B, and T, respectively, the six closest carbons, the two closest plus the four second closest, and the one closest plus three second closest are treated exactly. The remaining quadrupoles are treated as a continuum with the three lower limits s_m taken to bisect the appropriate carbon-carbon bonds, as shown in Fig. 1. For two different values of z, the contributions $F^{\mathrm{C}}(s_m\infty)$ to the field arising from the distant quadrupoles treated as a continuum and derived from Eq. (25) are presented in Table V together with the exactly calculated fields $F^{\mathrm{ex}}(s_m)$ created by the closest carbon atoms. For all six geometries considered, there is a very significant cancellation between the two contributions $F^{\mathrm{ex}}(s_m)$ and $F^{\mathrm{C}}(s_m\infty)$ which causes the total field $F=F^{\mathrm{ex}}(s_m)+F^{\mathrm{C}}(s_m\infty)$ to be much smaller. This cancellation occurs because Eq. (20) shows that, while the values arising from carbon atoms in the vicinity of the noble gas are negative, positive contributions are generated by more distant carbon atoms for which $(5\cos^2\theta_i - 3)$ is negative. Table IV compares with the results computed exactly using the GULP program, the energies $U_{\mathrm{QID}}(z,\mathbf{p})$ predicted through Eq. (19) using the total fields assembled in Table V. The differences between the two calculations arise because the GULP program does not use the point dipole and point quadrupole approxi-

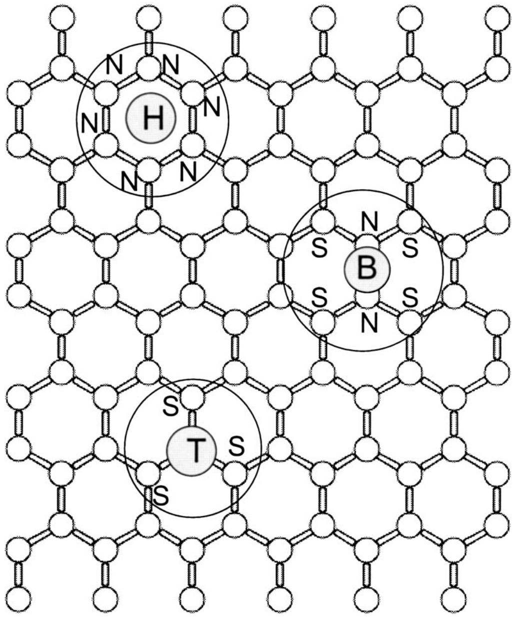

FIG. 1. Three positions of absorption of noble gas on graphite: above the center of the six membered ring H, above the center of the carbon-carbon bond B, and above the carbon atom T. N denotes the nearest carbon, S denotes second nearest carbon; distances outside circles are treated as continuum. At the top site T the first nearest carbon neighbor lies directly below the noble gas atom.

mations. However, this comparison shows that the analytic treatment does indeed reveal the origin of the very small values of $U_{\mathrm{QID}}(z,\mathbf{p})$. Thus, the minute values of these energies arise not only because F is small on account of the cancellations between its contributions from close and distant neighbors but also because $U_{\mathrm{QID}}(z,\mathbf{p})$ depends quadratically on this field. This last observation shows why the present results are not at variance with the previous findings[14] that the quadrupole moments of the carbon atoms are a significant factor in the absorption of water and nitrogen on graphite because the strengths of these latter two interactions are linear and not quadratic in the fields generated by the carbon quadrupoles.

If the lower limit of the integration in Eq. (23) is set to zero, thus treating the graphene sheet as a continuous distribution of quadrupoles, $U_{\mathrm{QID}}(z,\mathbf{p})$ is found to vanish. This shows that this interaction is only nonzero on account of the atomistic structure of the solid. This explains the negligibly small values of the computed $U_{\mathrm{QID}}(z,\mathbf{p})$. In the continuum limit, a graphene sheet becomes a collection of planes each having a uniform charge distribution. The field generated by each plane is a constant independent of z outside the sheet with the sum of the charges on all planes describing one graphene sheet being zero. Consequently the electric field outside the sheet is zero in this continuum description so that no dipole is induced on the noble gas atom with $U_{\mathrm{QID}}(z,\mathbf{p})$ being therefore predicted to vanish.

B. The full noble gas-graphite interaction

For the three possible positions of absorption ($\mathbf{p}=H$, B, and T) of a noble gas atom on a single graphene sheet, the predictions for the equilibrium value ($z_e(\mathbf{p})$) of z and the binding energy $D_e(\mathbf{p})(=-U_T(z_e,\mathbf{p}))$ calculated by including all the purely two-body interactions in Eq. (1) are presented in Table VI. Only the multibody Axilrod-Teller energy $U_{\mathrm{AT}}(z,\mathbf{p})$ and $U_{\mathrm{QID}}(z,\mathbf{p})$ are omitted. Since the latter energy was shown to be negligible, it was not included in any of the calculations to be described.

The cohesion is seriously underestimated, as manifested by too small predictions for $D_e(H)$ with those for $z_e(H)$ being too large, when N, the number of electrons used to construct the exchange functional, is taken to be 12. The predictions (Table VI) obtained by increasing N, therefore enhancing the magnitude of the attractive exchange contribution $V_{\mathrm{ex}}(r)$ to $V_s(r)$, differ significantly from those derived taking N to be 12. However, the results show that there is no value for N which will simultaneously reproduce the experimental values of $D_e(H)$ and $z_e(H)$. Thus, although for each system, an N value can be found which will reproduce either $D_e(H)$ or $z_e(H)$, it does not appear possible to correctly reproduce both of these quantities simultaneously.

The impossibility of finding a value for N which will simultaneously reproduce both $D_e(H)$ and $z_e(H)$ when only the two-body terms are considered indicates that the entire shapes of the predicted $U_T(z,\mathbf{p})$ are not correct and that these difficulties cannot be ascribed solely to problems of scale. The Axilrod-Teller energy $U_{\mathrm{AT}}(z,\mathbf{p})$ exhibits a very different type of dependence on z than the two-body terms as pointed out previously.[13] The results presented in Table VII derived from Eq. (1) by including both the two-body terms and $U_{\mathrm{AT}}(z,\mathbf{p})$ also show that the cohesion is still underestimated if N is taken to be 12. However, the results for $N=500$ do adequately reproduce the experimental data. This shows that the delocalized and mobile nature of the graphite π electrons does indeed become manifest in the short range repulsive interactions between noble gas atoms and graphite.

The $D_e(H)$ values presented in Table VII are larger than the early DFT predictions[67] by factors of about 3. It is now well established that such calculations significantly underestimate these cohesions because the local functional does not even implicitly describe the dispersive attractions which, furthermore, were not explicitly introduced. The defects of the early computations were rectified by a very recently pre-

TABLE V. Contributions to the electric field generated by carbon atom quadrupole moments (a.u.). For definitions of fields see text. Distances z in Å and lower boundary s_m for start of continuum treatment in a.u.

z	$H(s_m=3R_{\mathrm{CC}}/2)$		$B(s_m=3R_{\mathrm{CC}}/2)$		$T(s_m=\sqrt{7}R_{\mathrm{CC}}/2)$	
	$F^{\mathrm{ex}}(s_m)$	$F^{\mathrm{C}}(s_m^{\infty})$	$F^{\mathrm{ex}}(s_m)$	$F^{\mathrm{C}}(s_m^{\infty})$	$F^{\mathrm{ex}}(s_m)$	$F^{\mathrm{C}}(s_m^{\infty})$
3.0	−0.006 178	0.006 168	−0.006 388	0.006 168	−0.006 226	0.005 819
3.7	−0.003 926	0.003 614	−0.003 754	0.003 614	−0.003 319	0.003 239

TABLE VI. Binding predicted without inclusion of the Axilrod-Teller interaction. Binding energies in 10^{-3} eV and equilibrium separations z in Å with $\mathbf{p}=H$, B, or T. Experimental data from Ref. 74.

	Argon-graphite							
	D_e				z_e			
N	12	500	∞	Expt.	12	500	∞	Expt.
H	64.3	176.6	302.5	86.0	3.78	3.20	2.93	3.20
B	63.1	170.1	285.2		3.80	3.24	2.97	
T	63.3	170.2	285.1		3.80	3.25	2.98	
	Krypton-graphite							
	D_e				z_e			
N	12	500	∞	Expt.	12	500	∞	Expt.
H	81.2	223.8	384.4	160.0	3.92	3.30	3.01	3.35
B	80.3	217.3	367.8		3.93	3.34	3.05	
T	80.5	217.7	368.1		3.93	3.34	3.06	
	Xenon-graphite							
	D_e				z_e			
N	12	500	∞	Expt.	12	500	∞	Expt.
H	119.6	337.8	589.6	204.0	4.03	3.37	3.05	3.60
B	118.6	330.6	571.2		4.05	3.40	3.08	
T	119.0	331.4	572.3		4.05	3.40	3.09	

sented modification[68] of DFT. In the latter, the dispersive attractions are described using a nonlocal potential constructed as the sum of atomic contributions each of which contains adjustable parameters. This total potential is added to a standard DFT functional, with the sum of the two constituting the exchange-correlation potential acting on the electrons. The parameters entering the nonlocal potential generating the dispersive attractions were determined[68] by demanding that computational implementations of the theory reproduce the potential energy, that is the energy as a function of nuclear positions, already known independently from accurate *ab initio* calculations. Thus, the parameters for argon and carbon were derived from independently[69] determined results for the argon and benzene dimers, respectively. Such a dispersion corrected DFT computation for the absorption of argon on a single graphene sheet predicted[70] $D_e(H)$ and $z_e(H)$ values of 113 meV and 3.33 Å.

The results in Table VII predict in accordance with previous conclusions[71–73] that absorption occurs preferentially at the hole site, although this is favored over the bond site by only 4.4, 4.2, and 4.6 meV for Ar, Kr, and Xe, respectively. The top site is predicted to be only very slightly less favored than the bond site with corresponding excitation energies $D_e(H)-D_e(T)$, denoted ΔD_T, of 5.0, 4.7, and 5.3 meV. A low energy electron diffraction study[71] has provided direct experimental evidence that Xe is absorbed at the hole sites. The present results are consistent with the prediction[70] from the dispersion corrected DFT computations that, for Ar, both $D_e(H)-D_e(B)$, denoted ΔD_B and ΔD_T, are about 5.1 meV. For Kr and Xe, a combination[73] of two different analyses of experimental data yielded ΔD_B values of 5.8 and 6.5 meV, respectively, not dissimilar to the present results. This paper[73] also presented predictions for ΔD_B and ΔD_T deriving from both isotropic atom-atom potentials and some containing anisotropic terms. The results of 5.6, 5.9, and 5.9 meV for ΔD_B and 6.2, 6.5, and 6.6 meV for ΔD_T derived using the isotropic potentials are not out of line with any of the values just presented. However, these authors commented that the much larger results predicted with their anisotropic potentials, being inconsistent with the Kr and Xe 5.8 and 6.5 meV values deduced from experiment, could not be substantiated. Furthermore, the prediction[73] for Ar of 9.4 meV for ΔD_B is significantly larger than either the present (Table VII) result or the 5.1 meV value derived from the dispersion corrected DFT computation.[70] Since this computation takes full account of any anisotropy, it provides further evidence that this is overestimated in the model.[73] Furthermore, the similarity between the DFT and present (Table VII) predictions for ΔD_B provides evidence that anisotropy in the potentials is not important, thus indicating the utility of the present approach based on Eqs. (1) and (2).

For both $D_e(H)$ and $z_e(H)$, as well as the excitation energy ΔD_B, the similarity between the dispersion corrected DFT predictions and those of the present rather different approach is evidence for the reliability of both types of calculation. Furthermore, the observation[70] that the predictions re-

TABLE VII. Binding predicted with inclusion of the Axilrod-Teller interaction. See notes in Table VI.

	Argon-graphite							
	D_e				z_e			
N	12	500	∞	Expt.	12	500	∞	Expt.
H	30.5	111.0	207.5	86.0	3.98	3.32	3.03	3.20
B	29.8	106.6	196.4		4.00	3.37	3.08	
T	29.6	106.0	195.4		4.01	3.37	3.09	

	Krypton-graphite							
	D_e				z_e			
N	12	500	∞	Expt.	12	500	∞	Expt.
H	37.7	137.9	260.2	160.0	4.14	3.44	3.13	3.35
B	37.2	133.7	249.3		4.15	3.48	3.17	
T	36.8	133.2	248.2		4.16	3.48	3.18	

	Xenon-graphite							
	D_e				z_e			
N	12	500	∞	Expt.	12	500	∞	Expt.
H	58.4	213.7	406.1	204.0	4.25	3.53	3.18	3.60
B	57.8	209.1	393.3		4.26	3.55	3.21	
T	57.5	208.4	392.6		4.27	3.55	3.22	

mained essentially unchanged on adding second and third graphene sheets is good evidence that the results of the present calculations are comparable with the experimental data for the absorption of noble gases on solid graphite.

IV. CONCLUSIONS

There are three principle conclusions that emerge from this theoretical study of the interaction of a noble gas atom with graphite. The first of these is to emphasize the importance of the Axilord-Teller triple-dipole dispersion interaction whose significance for these systems has been elucidated previously.[13] Indeed, in the present approach, it is not possible to obtain a realistic description of the absorption on a unified basis unless this interaction is considered. The second conclusion is that the semiconducting and mobile nature of the graphite π electrons becomes manifested through the exchange functional in the DFT model used to compute the uncorrelated short range interaction between the noble gas atom and the graphite carbons. It is found that the value of the effective number of electrons N required to calculate this functional is large, in the region of 500, rather than being in the region of 12 that would be expected if the absorption could be described a sum of truly localized pairwise interactions. This suggests that it might be possible to glean information about the electronic structure of a material by investigating the value of N that is needed to reproduce structural information concerning either the pure material or the binding of absorbed species. The third conclusion of this study is that the energy, arising from the interactions between the permanent quadrupoles on the carbon atoms with the dipole they induce on the noble gas atom, is very small. It has been shown that this interaction is only nonzero on account of the atomistic structure of the graphene sheets.

The three factors elucidated here concerning the nature of the binding of a noble gas atom to graphite provide information essential for describing the interactions between the ions and the wall carbon atoms in the systems of ionic salts encapsulated in carbon nanotubes of current interest. The second conclusion is of particular importance, that concerning the value of N needed to construct the exchange functional entering the calculation of the short range interactions between the ions and wall atoms. This paper has also presented methods for describing the dispersive attractions between the ions and wall carbons including deriving the required parameters, such as the carbon electron number. Both the investigation[28] of KI and CsI crystals encapsulated in carbon nanotubes and ongoing studies relied heavily on the conclusions gleaned here concerning the nature of the interactions between noble gas atoms and graphite.

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